PATENT SPECIFICATION

(11) 1367941

(21) Application No. 48251/71 (22) Filed 18 Oct. 1971
(31) Convention Application No. 7015312 (32) Filed 19 Oct. 1970 in
(33) Netherlands (NL)
(44) Complete Specification published 25 Sept. 1974
(51) International Classification B07D 53/34
(52) Index at acceptance
C1A 3C2
B1L 5B2

(19)

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(54) PROCESS FOR THE REMOVAL OF SULPHUR COMPOUNDS FROM GASES OR GAS MIXTURES

(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organised under the laws of The Netherlands, of 30 Carel van Bylandtlaan, The Hague, The Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a process for the removal of sulphur compounds from gases or gas mixtures containing one or more gaseous sulphur compounds, the compounds being removed in the form of sulphur oxides.

A process has already been suggested for the removal of sulphur oxides from flue gases in which the said gases are freed from sulphur oxides by contacting these gases at temperatures in excess of 300°C with an acceptor for sulphur oxides which consists of a metal or a metal compound supported on a suitable carrier. In order to prevent the solid matter invariably present in flue gases, and consisting of soot and fly ash, from clogging the acceptor bed, the flue gases to be treated are passed through an apparatus provided with a system of parallel or at least substantially parallel gas channels, the walls of which are gas-permeable and behind which the acceptor material is present. The sulphur oxides to be removed diffuse through the walls of the gas channels and come into contact with the acceptor while the solid matter remains in the gas channels and is entrained with the flue gases flowing at a relatively high gas rate.

The above process is less attractive for the removal of sulphur oxides from off-gases which do not contain solid matter, such as off-gases from a Claus plant, since the features of the apparatus used are superfluous for such off-gases. It would be far more suitable to carry out the process using fixed acceptor beds. However, the difficulty then arises that the process requires that the sulphur oxides are accepted under oxidising conditions and that the metal applied to the acceptor for the acceptance of the sulphur oxides should be present in the form of oxide. By their nature flue gases possess a sufficient amount of free oxygen to meet both prerequisites in the contacting of these gases with the acceptor from the very beginning. On the other hand, Claus off-gases as are obtained after the last catalytic bed of a claus plant, not only contain sulphur dioxide, but also, for example, hydrogen sulphide; and they are free from oxygen. Such off-gases, after having passed a usual thermal or catalytic incinerator (combustion zone), do not contain sufficient oxygen to convert all the acceptor present to the oxide form at the very beginning of the process, so that at first sulphur dioxide slips through the acceptor bed.

It is an object of the invention to provide a "fixed-bed" process which is suitable for the purification of claus off-gases with the aid of solid acceptors for sulphur oxides. A further object is to provide a process in which, in addition, to sulphur oxides, other sulphur compounds such as hydrogen sulphide are also removed from the off-gases to be purified, which process can be carried out continuously.

For the sake of brevity a gas or gas mixture which contains one or more gaseous sulphur compounds and which is free from solid matter will be referred to herein "as the gas to be treated".

According to the present invention there is provided a process for treating a gas mixture which is free from solid matter to remove sulphur present therein as one or more gaseous sulphur compounds, said sulphur being removed in the form of sulphur oxide(s) by ab-

sorption of said sulphur oxide(s) on a metal-containing and/or metal compound-containing acceptor under oxidising conditions at a temperature of from 325°C to 475°C, said acceptor when loaded with sulphur oxide(s) being regenerated under reduced conditions at a temperature of from 325°C to 475°C, wherein the gas to be treated is supplied to one or more fixed beds of said acceptor in such a manner that (a) whilst a first part of said bed or a first one of said beds is contacted with the gas to be treated, a second part of said bed or a second one or said beds is contacted with a reducing gas or gas mixture and a third part of said bed or a third one of said beds is contacted with an oxidising gas or gas mixture, (b) when the acceptor comprising in said first part of said bed or said first bed has become loaded with sulphur oxide(s), said gas to be treated is supplied to said third part of said bed or said third bed, said first part of said bed or said first bed is contacted with said reducing gas or gas mixture and said second part of said bed or said second bed is contacted with said oxidising gas or gas mixture, and (c) when the acceptor comprised in said third part of said bed or said third bed has become loaded with sulphur oxide(s), said gas to be treated is supplied to said second part of said bed or said second bed, said third part of said bed or said third bed is contacted with said reducing gas or gas mixture and said first part of said bed or said first bed is contacted with said oxidising gas or gas mixture.

In order to prevent the various types of gas from contacting each other in a bed or a part thereof, which is undesirable from the point of view of operating efficiency and process safety, the process according to the invention is preferably carried out in such a way that, before a bed or part of a bed which has been in contact with a reducing gas is in turn contacted with the oxidizing gas, and/or before a loaded bed or part of a bed is contacted with a reducing gas, it is first contacted with an inert gas. The term "inert gas" means a gas which does not give any undesirable reactions with the gas present in the bed or part of the bed or with the gas to be subsequently introduced therein, while it should not affect in an undesirable manner the acceptor present in the bed or part of the bed. The free-oxygen content in such a gas should in general be low. The inert gas used may be, for example, nitrogen, carbon dioxide or steam, either separately or in combination.

The oxidizing gas may be any free oxygen-containing gas mixture. It is preferred, however, that such a gas does not contain above 10%, by volume, of free oxygen in order to prevent the acceptor becoming too hot resulting in its disintegration. A suitable gas mixture may be obtained by burning low boiling hydrocarbons, such as methane or natural gas, with oxygen or air in a slight excess with respect to the amount required for their complete combustion. This combustion gas also comprises a considerable amount of steam, about 66%, by volume, at most, which is particularly advantageous when the oxidizing gas after its passage through the acceptor bed to be oxidized is mixed with the reducing gas used for treating the loaded bed. For this particular further application of the oxidizing gas it should preferably comprise less than 2%, by volume, of oxygen after its passage through the acceptor bed. It is also possible to mix the off-gas emanating from the acceptor bed being oxidized and still containing free oxygen with the gases to be treated according to the process of the present invention. It will be clear that it is further possible to use such off-gas partially for both purposes mentioned.

Further addition of steam e.g. to an amount up to 90%, by volume, can be made to the oxidizing gas, particularly in the case where after its passage through the acceptor bed to be oxidized it is mixed with the reducing gas.

With a view to a prolonged acceptor life it is advantageous to pass the reducing gas through an acceptor bed or part of a bed countercurrent to the direction of flow of the gases to be treated. The other gases, viz. the gas to be treated, oxidizing gas and inert gas, can all be passed through an acceptor bed or part of a bed in the same direction. However, it is sometimes desirable to pass the oxidizing gas in counterflow too, for example, when treating Claus off-gases.

These latter off-gases are obtained from the Claus process at a temperature which is normally considerably lower than 325°C. By passing the oxidizing gas through the acceptor bed or part of a bed in counterflow to the Claus off-gases to be treated, it is ensured that the beginning of the said bed or part of the bed has a considerably higher temperature than the end thereof, so that the off-gases to be treated are heated up to the desired accepting temperature by the bed itself.

The process according to the invention may be carried out in various ways, viz. according to the "swing" method in which different beds are used alternately, semi-continuously or fully continuously. In the swing method it is preferred to use at least three separate acceptor beds. It is advantageous to use fixed beds with radial flow through the bed. It is also possible to use four acceptor beds arranged in pairs, the beds in each pair being arranged in parallel and being such that the total amount of time required for contacting an acceptor bed with a reducing gas and with an oxidizing gas and, optionally, also with an inert gas is no greater than and is preferably equal to the accepting time i.e. the time required for a bed to become loaded when contracted with the gas to be treated. This permits the swing method to be carried out in such a way that two beds

are each time contacted with the gases to be treated (the accepting phase), while the two remaining beds are contacted first with a reducing gas (the reducing phase) and then with an oxidizing gas (the oxidizing phase). For a semi-continuous operation of the process the various phases in the individual acceptor beds have been shifted in respect of each other.

In another embodiment of the process, one single fixed cylindrical acceptor bed is used which is divided into three acceptor zones which are not in communication with each other, which zones are successively contacted with the gas to be treated, the direction of rotation in respect of the successive contacting with the said gas being the same as that in which the said zones are contacted with the oxidizing gas.

For a continuous embodiment of the process according to the invention one single fixed cylindrical acceptor bed is used divided into a plurality of radial zones which are not in communication with each other, successive zones being continuously contacted with the gas to be treated in sequence, whereupon the zones which have been in contact with the manner indicated with the gas to be treated are regenerated in sequence by successively contacting them with the reducing gas and then with the oxidizing gas.

To prevent the various types of gas from being simultaneously introduced into the same zone(s), this continuous embodiment is preferably carried out in such a way that the part of the cylindrical acceptor bed which is being contacted with the gases to be treated is separated by at least one radial zone, and preferably by two or more radial zones, from the other part of the cylindrical bed which is being regenerated, the part of the cylindrical bed which is being contacted with an oxidizing gas during the regeneration being likewise separated by at least one radial zone, and preferably two or more radial zones, from the other part of the said bed which is contacted with a reducing gas during the regeneration.

The above embodiment permits continuous operation in that certain parts of the cylindrical acceptor bed divided into radial zones are continuously in the accepting phase or in a regeneration phase, the regeneration phase itself again being divided into two separate phases. By ensuring that at least one radial zone separates three various process phases, the various types of gas are also prevented from contacting each other via the acceptor bed and thus from causing undesirable reactions.

In order successively to contact the various zones with the various types of gas, the fixed acceptor bed may, for example, be rotatably arranged in a reactor housing. However, according to a preferred embodiment of the invention a stationary fixed acceptor bed is used while the gases are introduced in such a way that they come into contact with all zones in succession, as will be explained below in greater detail.

Since the use of metal- and/or a metal compound-containing acceptors requires the removal of sulphur compounds in the form of sulphur oxides under oxidative conditions, in other words in the presence of oxygen or an oxygen-containing gas, it is sufficient for that part of the cylindrical bed which is again contacted with the gases to be treated after regeneration to be separated by only one zone from that part of the said cylindrical bed which is contacted with an oxidizing gas during the regeneration.

The gases or gas mixtures which contain gaseous sulphur compounds and are free from solid matter may contain hydrogen sulphide and/or sulphur dioxide. Surprisingly, it has been found that under the acceptance conditions used in accordance with the invention hydrogen sulphide is removed in the form of sulphur dioxide. This has the great advantage that, for example, the off-gases of sulphur-producing installations according to the Claus process can be directly subjected to a process according to the invention, eliminating the usual incinerator for such off-gases. Oxygen or an oxygen-containing gas, such as air, should then be added to such off-gases to provide for the oxidative medium. However, it remains possible, if desired for certain reasons, first to incinerate the off-gases from the said installations in a thermal or catalytic incinerator and then to subject the incineration gases which are now free from hydrogen sulphide to a process according to the invention after addition of an additional amount of oxygen or an oxygen-containing gas.

If the Claus off-gases have been subjected to incineration said gases should be cooled to the temperature range at which the present process is carried out. Cooling may be effected by indirect heat exchange or by injection of steam or water into the hot gases. A particular advantageous method is to combine the incinerated Claus off-gases with a flue gas. As the latter contains free oxygen, combining of both gases serves a dual purpose, i.e. cooling of the hot (Claus) gases and providing the required oxygen for acceptance. The flue gas is preferably freed from particulate matter by electrostatic precipitators. The Claus gases are suitable diluted in an amount of from 0.02—1.0 parts, by volume, per part, by volume, of flue gas.

It is possible that the gases to be treated only contain hydrogen sulphide or other sulphur compounds which can be readily oxidized to sulphur oxides over a metal compound. Gases containing insufficient oxygen as a result of the mode of their preparation should be mixed with free oxygen or a free oxygen-containing gas before being subjected to the

process of the invention. A possible way of providing the free oxygen has already been set out hereinbefore.

The acceptors used according to the invention preferably contain copper and/or copper oxide as the metal and/or the metal compound. The carrier material used is preferably activated alumina such as gamma-alumina, or a mixture of gamma- and alpha-alumina, although in principle all solid materials may be considered which are temperature-resistant and are hardly, if at all, affected by sulphur oxides under the conditions prevailing. As examples may be mentioned bauxite, silica-alumina and silica-magnesia.

Acceptors consisting of copper and/or copper oxide supported on, preferably active, alumina as carrier have beun found to be very suitable for the removal of sulphur dioxide from gases under oxidative conditions at temperatures in excess of 300°C. Under the conditions at which sulphur dioxide is chemically bound by the acceptor sulphur trioxide is also removed from the gases, while, as stated above, it was also found that hydrogen sulphide is oxidized to sulphur dioxide which is subsequently accepted.

The copper content of the acceptor may, also depending on the specific surface of the material used, vary within wide limits. As a rule this content amounts to 1—15%, by weight, based on the finished acceptor. Optimum results are obtained with acceptors containing 4—10%, by weight, of copper.

Mechanically strong acceptors containing 1—6%, by weight, of glass in the carrier material are obtained by mixing carrier material and a pulverized glass, e.g. glass flour, glass powder or glass frits, together with a suitable binder; forming the mixture into a desired shape; and subsequently calcining the shaped material (extrudates, globules, pills or possibly ceramic castings) at temperatures in excess of 780°C and preferably at temperatures of from 800 to 1300°C. After calcining and cooling, the desired metal compound is applied by means of impregnation. Calcining is then repeated, this time at temperature of from 500°C to 600°C.

The great advantage of acceptors of the above type resides in the fact that they can be regenerated after having been loaded with sulphur oxides (with formation of metal sulphate) at a temperature equal or practically equal to that at which acceptance took place. Operating at acceptance and regeneration temperatures which hardly differ is not only an advantage from the point of view of heat economy, but is also of great importance for the life of the acceptor. It is economically essential that the acceptor used should be capable of being regenerated several hundreds of times or more without losing too much stability and activity. It is not easy to achieve such a long life with acceptors which have to be heated and/or cooled over a relatively wide temperature range per regeneration, since the chemical and physical stability of the metal-and/or metal compound-containing acceptor can be seriously impaired by this kind of temperature change.

The removal of sulphur compounds in the form of sulphur oxides under oxidising conditions in the presence of free oxygen, takes place at temperatures of from 325°C to 475°C. It is preferred to use temperatures of from 375°C to 430°C. Regeneration under reducing conditions is effected in the same temperature range. Acceptance and reduction are preferably carried out within this range at the same or practically the same temperature. This is understood to mean that reduction follows acceptance without interim cooling or warming-up of the acceptor bed or part of this bed. It should be noted that in practice local temperature fluctuations of 50°C or more can readily occur during acceptance, and the temperature of the bed or part of the bed will usually be higher towards the end of the acceptance than at the beginning thereof. The heat generated as a result of exothermic reactions during the acceptance can be removed by introducing colder regeneration gas.

The reducing gas used for the regeneration may be hydrogen or hydrogen and/or carbon monoxide-containing gas mixtures. It is also possible to use light hydrocarbons or mixtures thereof, such as methane, ethane, propane or technical mixtures, such as natural gas or tops obtained in the direct distillation of petroleum. If desired, these reducing gases may be used diluted with inert gases such as nitrogen and/or water vapour, or with the oxidizing gas of low oxygen content emanating from the acceptor bed being oxidized as explained hereinbefore.

In the regeneration as used according to the process of the invention two steps are to be distinguished. In the first step the metal sulphate-loaded acceptor is treated with the reducing gas. Metal and/or metal sulphide are mainly formed in addition to a small amount of metal oxide. In the second step metal and/or metal sulphide are oxidized. When the metal used is copper, the following reactions take place during the oxidation step:

$$Cu + \tfrac{1}{2}O_2 \rightarrow CuO$$
$$Cu_2S + 2\tfrac{1}{2}O_2 \rightarrow CuO + CuSO_4$$

After the oxidation step the acceptor is ready for the acceptance of new amounts of sulphur oxides. As can be seen from the above reaction equations, it is advantageous to carry out the regeneration in such a way that the Cu_2S content after the reduction step is as small as possible, since half the copper bound as sulphide is withdrawn from the acceptance of sulphur oxides.

Acceptance is effected under oxidising conditions; the free oxygen content in the gas to be treated is preferably such that after conversion of gaseous sulphur compounds other than sulphur oxides to sulphur dioxide, the molar ratio between the free oxygen still present and the total amount of sulphur dioxide present is 1 or more than 1. On the other hand, because of cost-saving considerations, the amount of oxygen will generally not be much greater than is stoichiometrically required for the conversion to sulphur oxides and acceptance as such of all gaseous sulphur compounds.

It is noted that in the regeneration of the acceptor loaded with metal sulphate a gas evolves having a relatively high concentration of sulphur dioxide. Consequently, the process according to the invention is very suitable for treating large amounts of gases or gas mixtures containing relatively low concentrations of gaseous sulphur compounds. The sulphur dioxide-rich gas may then be processed to elemental sulphur or sulphuric acid in any known manner. If the process according to to the invention is used for Claus off-gases, the sulphur dioxide-rich regeneration gas may be returned to the Claus process proper in a simple manner.

It is sometimes advantageous in the further processing of the freed sulphur dioxide to cool the sulphur dioxide-rich gas obtained in the regeneration to such an extent that a condensate is formed and to strip the resultant condensate with steam in order to liberate the sulphur dioxide from it.

The invention also includes a process as defined above which is carried out in apparatus comprising a cylindrical housing divided internally into at least three acceptor-containing compartments which are not in communication with each other, which compartments are each provided at the top/bottom of the housing with a supply/discharge opening which have a common gas inlet/gas outlet, and which openings are provided in the top/bottom in such a way that they can be sealed in a gas-tight manner by a rotatable disc at the inlet side of the housing and a similar disc at the outlet side of the housing, each of which discs is provided with one opening which as the disc is rotated corresponds with the respective opening or a part of the respective opening of each of said compartments in turn, the arrangement being such that in any given position of the discs the openings of the discs correspond with the openings of the same compartment. The said rotatable disc is preferably arranged on the outer surface of the cylindrical housing within the gas inlet/gas outlet to which end the inlet/outlet has a conical shape while its widest edge is connected to the top or bottom of the housing, respectively. The openings in the rotatable discs and the compartments may have any desired shape. They are preferably curved and slot-shaped and extend over an arc of approximately 120°. As a rule circular openings will only be used for the rotatable discs and not for the compartments. In order to be capable of rotating the rotatable discs after the acceptor in a compartment has been loaded, the apparatus is also provided with means for rotating the discs in the same position relative to each other. In addition, each compartment should be provided with at least one extra gas inlet/gas outlet for the reducing and oxidizing gas required for the regeneration of the acceptor, as well as for the inert gas.

An apparatus of the type described above is represented in Figs. 1 and 2 of the accompanying drawings.

The continuous embodiment of the process according to the invention may be suitably carried out in an apparatus comprising a cylindrical housing, the inside of which contains a plurality of radial compartments which are not in communication with each other, a plurality of separate gas inlets for the gas to be treated, the reducing gas or gas mixture and the oxidizing gas or gas mixture, respectively, and a plurality of separate gas outlets for the said gases, respectively, and means for connecting each of said compartments in turn with said inlet(s) and said outlet(s) for the gases or gas mixtures mentioned. Said means can consist of two discs which can be rotated in such a manner as to maintain a fixed position relative to each other, each of which discs is provided with two or more curved slot-shaped openings, the disc being arranged in the upper part of the cylindrical housing and the other one at the bottom thereof, each disc sealing the said compartments in a gas-tight manner on one side and on the other side forming the boundary of a system of three or more concentric annular channels, which systems are located between the respective disc and the upper and lower surfaces of the cylindrical housing, and each of the annular channels of which systems is connected with a respective one or ones of said separate gas inlet(s) and gas outlet(s), the slot-shaped openings extending in any given position of the discs over a part of the radial compartments and being arranged in such a way that each opening corresponds with only one channel, while the slot-shaped openings in the upper and lower discs are in general alignment with each other. The rotatable discs are preferably coupled to a rotatable shaft adapted to be driven and disposed in the interior of the cylindrical housing.

Since it is possible to form a mixture of several types of gas after discharge from the acceptor bed(s) or parts thereof, one of the rotatable discs preferably has three slot-shaped openings extending over a number of compartments and the other disc at least two

of such openings. Identical numbers of channels should correspond with these openings. One of the discs preferably has two long openings and one short opening, which latter opening is specially meant for the introduction of an oxidising gas into the cylindical housing for a short period of time. In order to be able to introduce an inert gas as well, the system of circular channels at the gas inlet side of the housing preferably comprises four channels with matching gas inlets.

Since some types of gas can be discharged together, the corresponding slot-shaped openings in the upper and lower discs may be unequal in length. In this way the inert gas introduced may be discharged through the gas outlet for another type of gas. In order to be able to introduce inert gas after the acceptance phase and before the oxidation phase, one of the discs is also provided with two short openings arranged practically diametrically opposite each other, which both correspond with the smallest channel of the system of four channels, the gas inlet of this channel being connectable by means of these openings and the slot-shaped openings in the other disc either with the gas outlet of the outer channel or with the gas outlet of the inner channel of the other system of concentric circular channels.

In this way the inlet of the circular channel with which the short, slot-shaped opening corresponds may also be partially connected to the outlet of the central channel of the other system of concentric circular channels and partly to the outlet of one of the other channels of the latter system.

An apparatus of the above type as shown in Figs. 3—6 of the accompanying drawings.

The invention will be further elucidated with reference to the accompanying drawings, in which:—

Fig. 1 represents an apparatus suitable for use in the process according to the invention and containing three separated acceptor beds.

Fig. 2 is a cross-section of the apparatus of Fig. 1 taken on line A—A'.

Fig. 3 is a diagrammatic representation of an apparatus containing a plurality of radial compartments for acceptor material which are not in communication with each other.

Fig. 4 is a top plan view of the upper rotatable disc of the apparatus according to Fig. 3.

Fig. 5 is a top plan view of the lower rotatable disc of the apparatus according to Fig. 3.

Fig. 6 is a top plan view in partial crosssection of the apparatus according to Fig. 3.

Referring to Fig. 1A, the numeral 1 represents a cylindircal reactor divided into three compartments which are not in communication with each other by means of three partitions which are radially arranged and extend in the reactor from an upper surface 3 to a lower surface 4. Broken lines 2*a*, 2*b* and 2*c* represent the boundaries of these vertically arranged partitions with the cylindrical side wall of the reactor 1. Both the upper surface 3 and the lower surface 4 of each of these compartments containing solid acceptor are provided with at least one opening for the supply/discharge of the gases to be treated. The gases to be treated are supplied via a line 5 which is connected to a conically widening extension 6 forming the gas inlet. The conical extension 6 is sealed in a gas-tight manner by a rotatable disc 7 which, as will be discussed below, is provided with one single opening. Depending on the position of this rotating disc 7, it will be possible for the gases to be treated to be introduced first into one compartment and then into another compartment by means of this rotatable disc which seals the said compartments in a gas-tight manner. For the discharge of the gases to be treated the lower part of the reactor is provided with the same means as for the supply of the gases to be treated. As will be understood by those skilled in the art, it is, therefore, also possible to reverse the direction of flow of the gases through the reactor. A rotatable disc 8 which is provided with a single opening seals the lower side of the compartments in a gas-tight manner. The position of the lower disc will be in agreement with that of the upper disc 7, so that the gases introduced into a certain compartment can leave it at the other side via the opening in the lower surface 4 and the rotatable disc 8. The treated gases thus enter a conically shaped extension 9 forming the gas outlet and are discharged via a line 10. In Fig. 2 identical parts have been given the same reference numerals. The numeral 3 represents the upper surface of the cylindrical reactor 1. The disc 7 is secured onto this upper surface 3 in a rotatable and gas-tight manner. The broken lines 2*a*, 2*b* and 2*c* are the partitions which divide the interior of the reactor 1 into three equal compartments which are not in communication with each other. The upper surface 3 of each compartment is provided with a curved, slot-shaped opening 20 extending over an arc of approximately 120°. The rotatable disc 7 is provided with an identical opening 21 and in the position shown the gases to be treated are introduced into the compartment bounded by the partition 2*a* and 2*c*.

The disc 7 may be connected to the disc 8 at the other side of the reactor by means of a shaft, the opening in the latter disc being in line with the opening of the disc 7, so that the gases to be treated may flow through the compartment which is now open. In Fig. 2 the reference numeral 22 represents the passage for the said shaft.

When the acceptor has been loaded in a certain compartment, the disc 7 and the disc 8 coupled therewith are rotated over 120°

so that the next compartment is opened for the gases to be treated. The direction of rotation will be such that the compartment opened contains acceptor which has been previously contacted with an oxidizing gas. The selected embodiment of the apparatus ensures that at least the acceptance of the sulphur oxides takes place continuously.

To regenerate the loaded acceptor the reactor 1 is provided with at least one gas inlet 12 and one gas outlet 16 for each of the three compartments. In the embodiment shown the reducing gas, oxidizing gas and inert gas (steam) required for the regeneration are supplied through 13, 15 and 14 and discharged through 19, 17 and 18. The various lines are provided with the essential valves, use being made of the same inlet/outlet. It is of course also possible to introduce each of the said gases through its own inlet and to discharge it through its own outlet.

The rotatable discs 7 and 8 may be rotated after each acceptance with the aid of any means known *per se*. These means have been omitted in the diagrammatic drawing. It is also possible to design the conical extensions 6 and 9 in such a way that they cover the said rotatable discs and form a direct gas-tight connection with the upper surface 3 and the lower surface 4 of the reactor. It is also possible to use circular openings instead of the openings shown. A reactor thus modified is shown in Fig. 1B, wherein a part of the upper conical extension and of the cylindrical side wall are given in cross-section to show the rotatable disc and a compartment bounded by two radially arranged partitions. It will be clear to those skilled in the art that in order to prevent acceptor material from falling out of the compartments, the latter are provided with the required grids or other appropriate means.

Referring to Fig. 3, the numeral 39 represents the cylindrical housing of the apparatus, the centre of which is an unclosed cylindrical hollow space 37 bounded by a wall 34. The top and bottom of the acceptor space 33 are sealed by rotatable discs 38 and 41 provided with slot-shaped openings (see Fig. 4 and Fig. 5). The lower disc 38 has two large curved, slot-shaped openings 39 and 40 and a smaller opening 77, while the upper disc has two large and one smaller slot-shaped openings 42, 43 and 81. The upper disc also has two small openings 84*a* and *b* arranged practically diametrically opposite each other. The said openings of the upper disc correspond with four annular channels 44, 45, 46 and 47 arranged between the rotatable disc 41 and the upper wall 31 of the cylindrical housing 29. These annular channels are formed and bounded by the outer cylinder wall 30, partitions 48, 49 and 50, and the inner cylinder wall 34. Each annular channel has a plurality of inlets/outlets for gases; inlet/outlet 52 belongs to channel 44, inlet/outlet 56 to channel 45, inlet/outlet 53 to channel 46 and inlet/outlet 54 to channel 47. In the position of disc 41 shown, the cylinder space 33*b* is in open connection with the channel 47 through the opening 42 in the disc; the cylinder space 33*a* is likewise in open connection with the channel 44 through the opening 43 in the same disc. The remaining channels of the system are sealed in a gas-tight manner by means of sealing rings 61*b* pressing against the lower surface and sealing rings 61*a* pressing against the upper surface of the disc 41, which rings are arranged in annular trusses 57, 58*a*, 58*b*, 58*c* and 59.

Similarly, the openings of the lower disc correspond with a system of annular channels present between the rotatable disc 38 and the lower wall 32 of the cylindrical housing 29. These lower annular channels are formed by the outer cylinder wall 30, intermediate panels 82 and 83 and the inner cylinder wall 34. Each annular channel has an inlet/outlet for gases; inlet/outlet 66 belongs to channel 63, inlet/outlet 68 to channel 64 and inlet/outlet 67 to channel 65. In the position of the disc 38 shown, the cylinder space 33*b* is in open connection with the channel 65 via the opening 39; similarly the space 33*a* is in open connection with the channel 63 through the opening 40 in the disc. The other channels are sealed in a gas-tight manner by means of sealing rings 72*b* pressing against the upper surface and sealing rings 72*a* pressing against the lower surface of the disc 38, which rings are arranged in annular trusses 69, 70*a* and *b*, and 71.

The rotatable discs 38 and 41 are forcibly pressed against the sealing rings 72*b* and 61*b* by means of a pressing mechanism 51. This pressing mechanism 51 may consist of a small spring-loaded wheel, a number of which have been arranged on the outer and inner periphery of the said discs.

It is noted that the discs 41 and 38 in Figs. 4 and 5 are shown in the position in which gases supplied via a certain opening may flow through a certain part of the cylinder space divided into compartments which are not in communication with each other and may leave this space at the opposite side through a corresponding opening. As a result of the fact that during operation the two discs rotate continuously but remain in the same position relative to each other, other parts of the total acceptor bed are each time contacted with the gases supplied. The gas supplied is distributed in the compartments by means of distributing plates 62 arranged for the purpose. These plates 62 should also prevent acceptor from leaving the acceptor space with gas supplied from below. Grids 85 are arranged in the lower part of the compartments to prevent acceptor from leaving the acceptor space.

Referring to Fig. 6 which is a cut-away view

to show several sections, the numeral 85 represents a radial compartment. The internal cylinder space is divided into a plurality of such compartments, which compartments are bounded by gas-impermeable walls 86. The radial compartments extend to the inner cylinder wall 34 bounding the cylindrical hollow space 37. The annular trusses 57, 58*a*, *b* and *c* and 59 extend over the compartments 85, which trusses are interconnected by radial trusses 60 arranged over the gas-impermeable walls 86. The mutual distances between the annular trusses are such that they equal the width of the annular channels 44, 45, 46 and 47. The rotatable disc (not shown) rotates over these trusses. The top of the reactor is sealed by the upper wall 31 and provided with a plurality of inlets/outlets 52, 53, 54 and 56 for the various channels.

The rotatable discs 38 and 41 are rotated by means of a driving mechanism 73 (see Fig. 3) which, by means of a shaft 73*a*, bevel gears 73*b* and 73*c*, a shaft 73*d* and a gear 73*e* meshes with a toothed ring 73*f* arranged on the rotatable disc 38 near the cylindrical wall 34. Similar auxiliaries are also present for the rotatable disc 41. The shaft 73*a* extends in a shaft 74 which runs through the hollow space 37 in eccentric arrangement and is provided with a bevel gear 74*a*. The gear 74*a* meshes with a toothed ring 74*e* by means of a bevel gear 74*b*, a shaft 74*c* and a gear 74*d*. The shafts 73*d* and 74*c* run through the openings 35 and 36 in the cylindrical inner wall 34 in a gas-tight manner.

WHAT WE CLAIM IS:—

1. A process for treating a gas or gas mixture which is free from solid matter to remove sulphur present therein as one or more gaseous sulphur compounds, said sulphur being removed in the form of sulphur oxide(s) by absorption of said sulphur oxide(s) on a metal-containing and/or metal compound-containing acceptor under oxidising conditions at a temperature of from 325°C to 475°C, said acceptor when loaded with sulphur oxide(s) being regenerated under reducing conditions at a temperature of from 325°C to 475°C, wherein the gas to be treated is supplied to one or more fixed beds of said acceptor in such a manner that (a) whilst a first part of said bed or a first one of said beds is contacted with the gas to be treated, a second part of said bed or a second one of said beds is contacted with a reducing gas or gas mixture and a third part of said bed or a third one of said beds is contacted with an oxidising gas or gas mixture, (b) when the acceptor comprised in said first part of said bed or said first bed has become loaded with sulphur oxide(s), said gas to be treated is supplied to said third part of said bed or said third bed, said first part of said bed or said first bed is contacted with said reducing gas or gas mixture and said second part of said bed or said second bed is contacted with said oxidising gas or gas mixture, and (c) when the acceptor comprised in said third part of said bed or said third bed has become loaded with sulphur oxide(s), said gas to be treated is supplied to said second part of said bed or said second bed, said third part of said bed or said third bed is contacted with said reducing gas or gas mixture and said first part of said bed or said first bed is contacted with said oxidising gas or gas mixture.

2. A process as claimed in claim 1, wherein before a bed or part of a bed is contacted with said oxidizing gas or gas mixture, it is first contacted with an inert gas (as hereinbefore defined).

3. A process as claimed in claim 1 or claim 2, wherein before a loaded bed or part of a bed is contacted with said reducing gas or gas mixture, it is first contacted with an inert gas (as hereinbefore defined).

4. A process as claimed in claim 2 or claim 3, wherein the inert gas is nitrogen, carbon dioxide or steam.

5. A process as claimed in any one of claims 1—4, wherein the direction of flow of said reducing gas or gas mixture through a bed or part of a bed is countercurrent to the direction of flow of the gas to be treated.

6. A process as claimed in any one of claims 1—5, wherein the direction of flow of said oxidizing gas or gas mixture through a bed or part of a bed is countercurrent to the direction of flow of the gas to be treated.

7. A process as claimed in any one of claims 1—6, wherein at least three separate acceptor beds are used.

8. A modification of the process as claimed in any one of claims 1—6, wherein two pairs of acceptor beds are provided, the beds in each pair being arranged in parallel and being such that the total time required for effecting the required sequential steps of contacting a loaded bed with said reducing gas or gas mixture and with said oxidising gas or gas mixture and, optionally, also with said inert gas, is no greater than the time required for a bed to become loaded when being contacted with the gas to be treated, and wherein the gas to be treated is supplied to a first pair of beds whilst the second pair of beds is undergoing said sequential steps and thereafter the gas to be treated is supplied to said second pair of beds whilst said first pair of beds is undergoing said sequential steps.

9. A process as claimed in any one of claims 1—6, wherein a cylindrical acceptor bed is used, said bed being divided into three adjoining parts which are not in communication with each other, and wherein the gas to be treated is supplied in turn to each of said parts.

10. A process as claimed in any one of claims 1—6, wherein a cylindrical acceptor

bed is used, said bed being divided into a plurality of radial zones which are not in communication with each other, three such zones or groups of adjoining zones forming at any instant in the process said first, second and third parts of said bed, respectively, and said parts being progressively formed by different zones or groups of adjoining zones during the course of the process.

11. A process as claimed in claim 10, wherein at any given instant said first, second and third parts of the bed are separated from each other by at least one radial zone.

12. A process as claimed in claim 10 or claim 11, wherein at any given instant the part of the cylindrical bed which after regeneration is again contacted with the gas to be treated is separated by one radial zone from that part of the cylindrical bed which is being contacted with said oxidizing gas or gas mixture.

13. A process as claimed in any one of claims 1—12, wherein the gas to be treated is a gas containing hydrogen sulphide and/or sulphur dioxide, said gas also containing additional free oxygen when hydrogen sulphide is present therein.

14. A process as claimed in claim 13, wherein the gas to be treated is a Claus off-gas to which free oxygen or a free oxygen-containing gas has been added.

15. A process as claimed in any one of claims 1—13, wherein the gas to be treated contains free oxygen in amount such that after the conversion of gaseous sulphur compounds other than sulphur oxides to suphur dioxide, the molar ratio between the free oxygen still present and the total amount of sulphur dioxide present is 1 or more than 1.

16. A process as claimed in any one of claims 1—15 and substantially as hereinbefore described with reference to Figures 1 and 2 or Figures 3—6 of the accompanying drawings.

17. A process as claimed in any one of claims 1—6, which is carried out in apparatus comprising a cylindrical housing, the interior of which is divided internally into at least three acceptor-containing compartments which are not in contact with each other, which compartments are each provided at the top/bottom of the housing with a supply opening/discharge opening having a common gas inlet/gas outlet, and which openings are arranged in the top/bottom in such a way that they can be sealed in a gas-tight manner by a rotatable disc at the inlet side of the housing and a similar disc at the oulet side of the housing, each of which discs is provided with one opening which as the disc is rotated corresponds with the respective opening or a part of the respective opening of each of said compartments in turn, the arrangement being such that in any given position of the discs the openings in the two discs correspond with the openings of the same compartment.

18. A process as claimed in claim 17, wherein the rotatable disc is arranged on the outer surface of the cylindrical housing within the gas inlet/gas outlet, to which end the gas inlet/gas outlet has a conical shape, its widest edge being connected to the top or the bottom of the housing, respectively.

19. A process as claimed in claim 17 or claim 18, wherein the openings in the rotatable discs and in the compartments are curved and slot-shaped and extend over an arc of approximately 120°C.

20. A process as claimed in any one of claims 17—19, wherein the apparatus is provided with means for rotating the discs in the same position relative to each other.

21. A process as claimed in claim 17 and substantially as hereinbefore described with reference to Figures 1 and 2 of the accompanying drawings.

22. A process as claimed in any one of claims 1 to 6 which is carried out in apparatus comprising a cylindrical housing, the interior of which contains a plurality of radial compartments which are not in communication with each other, a plurality of separate inlets for the gas to be treated, the reducing gas or gas mixture and the oxidizing gas or gas mixture, respectively, a plurality of separate gas outlets for the treated gas, the reducing gas or gas mixture and the oxidizing gas or gas mixture, respectively, and means for connecting each of said compartments in turn with said inlet(s) and said outlet(s) for the gases or gas mixtures.

23. A process as claimed in claim 22, wherein said means consist of two discs which can be rotated in such a manner as to maintain a fixed position relative to each other, each of which discs is provided with two or more curved slot-shaped openings, one disc being arranged at the top of the cylindrical housing and the other at the bottom thereof, each disc sealing the said compartments in a gas-tight manner at one side and forming the boundary of a system of three or more concentric annular channels at the other side, which systems are located between the respective disc and the upper and lower surfaces of the cylindrical housing, and each of the annular channels of which systems is connected with a respective one or ones of said separate gas inlet(s) and gas outlet(s), the slot-shaped openings extending in any given position of the discs over a part of the radial compartments and being arranged in such a way that each opening corresponds with the one channel, while the slot-shaped openings in the upper and lower discs are in general alignment with each other.

24. A process as claimed in claim 23, wherein the rotatable discs are coupled to a rotat-

able shaft adapted to be driven and disposed in the interior of the cylindrical housing.

25. A process as claimed in claim 23 or claim 24, wherein one rotatable disc has at least three slot-shaped openings extending over a number of compartments and the other disc has at least two such openings.

26. A process as claimed in claim 25, wherein one rotatable disc has two long openings and one short slot-shaped opening.

27. A process as claimed in any one of claims 23—26, wherein the system of circular channels at the gas inlet side of the housing consists of four channels with gas inlets appertaining thereto.

28. A process as claimed in any one of claims 23—27, wherein the length of each of the slot-shaped openings of the discs which are in general alignment with each other is different.

29. A process as claimed in claim 27 or claim 28, wherein the upper disc is provided with two short slot-shaped openings positioned substantially diametrically opposite each other in such a manner as to correspond with the smallest channel of the system of four channels whereby the gas inlet of this channel can be connected, by means of said slot-shaped openings in said disc and the slot-shaped openings in the lower disc, either with the gas outlet of the outer channel or with the gas outlet of the inner channel of the other system of concentric circular channels.

30. A process as claimed in any one of claims 26—29, wherein the inlet of the circular channel with which the short slot-shaped opening corresponds is partly connected with the outlet of the central channel of the other system of concentric circular channels and partly with the outlet of one of the other channels.

31. A process as claimed in claim 22 and substantially as hereinbefore described with reference to Figures 3—6 of the accompanying drawings.

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Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1974.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1367941 COMPLETE SPECIFICATION

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Sheet 1

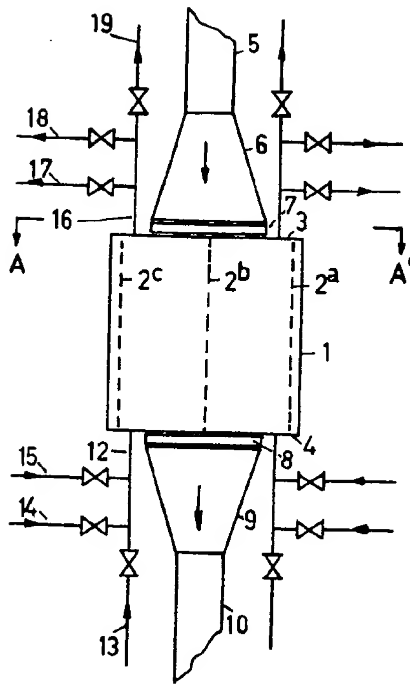

FIG.1A

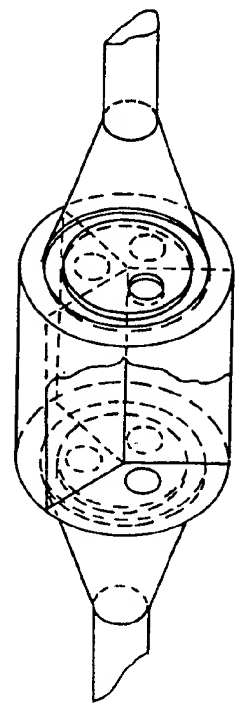

FIG.1B

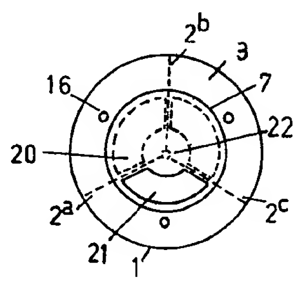

FIG.2

1367941 COMPLETE SPECIFICATION

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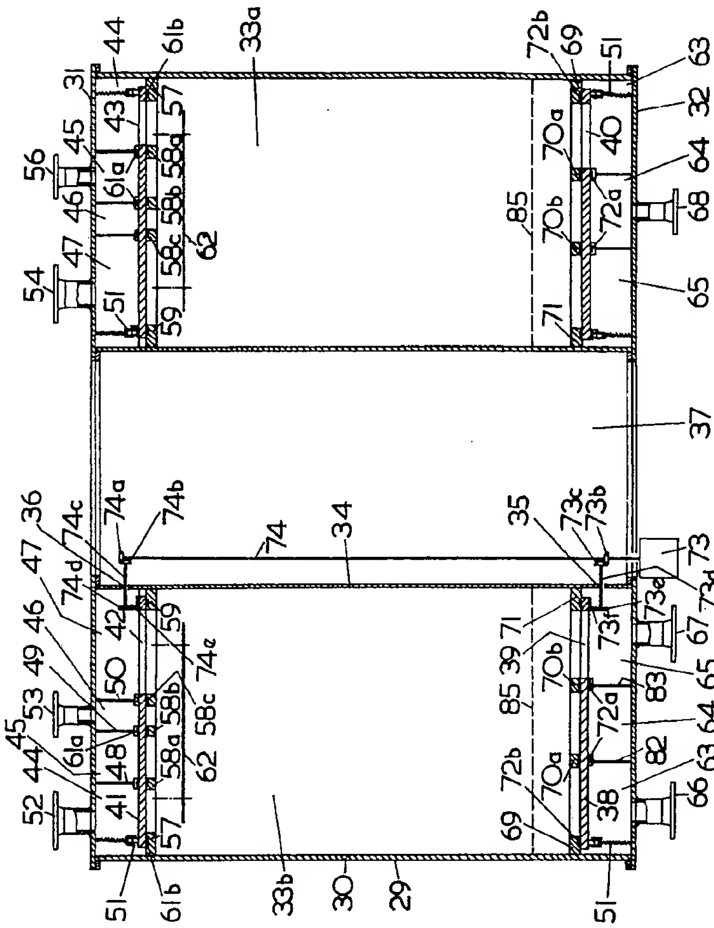

FIG. 3

1367941 COMPLETE SPECIFICATION
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Sheet 3

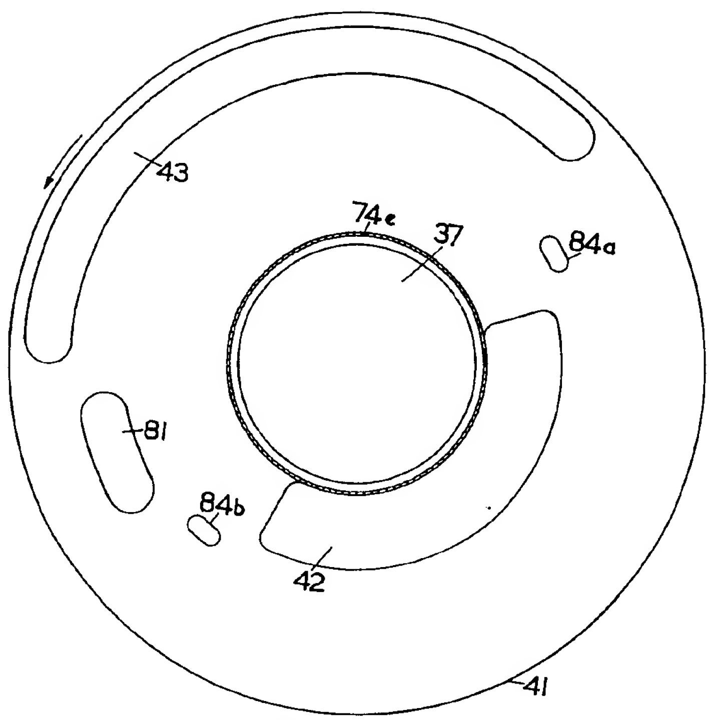

FIG. 4

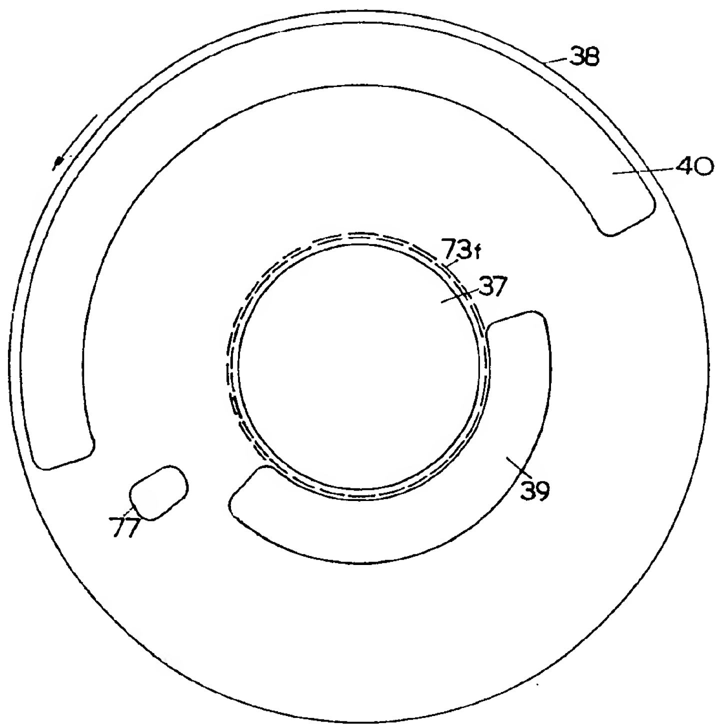

FIG. 5

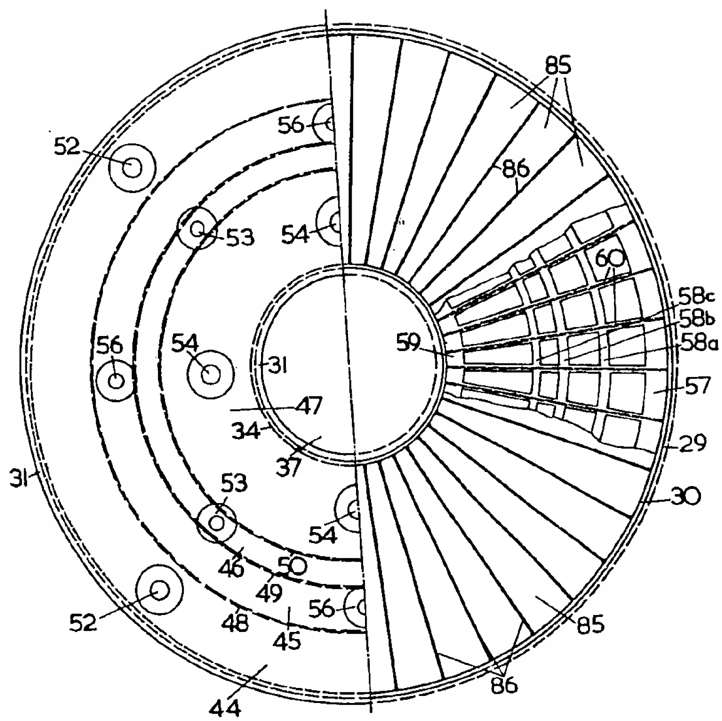
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FIG. 6